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(54) COATING COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a stably coatable coating composition capable of giving scuff-resistant coating films without using hard, entirely spherical particles.

SOLUTION: This coating composition comprises (A) 5–35 wt.% of inorganic microparticles, pref. alumina-based particles 3–50 μm in average size, with a Wadell practical sphericity of 0.70–0.99 and Knoop hardness of 1,300–8,000 kg/mm², (B) 45–95 wt.% of an active energy ray-reactive resin and (C) 0.2–10 wt.% of a dispersant, pref. an anionic one (based on a total weight of the components A to C).

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CLAIMS

[Claim(s)]

[Claim 1] Whenever [practical use spherical / Wadell] are 0.70–0.99, and it is 2 1,300–8,000kg [/mm] Knoop hardness. Constituent for coatings with which it consists of non-subtlety (particle A) activity energy-line reactivity resin (B) and a dispersant (C), and (A) is characterized by (B) being [45 – 95 % of the weight and (C)] 0.2 – 10 % of the weight five to 35% of the weight based on the sum total weight of (A) – (C).

[Claim 2] The constituent for coatings according to claim 1 whose mean diameter of ** (A) is 3–50 micrometers.

[Claim 3] The constituent for coatings according to claim 1 or 2 whose ** (A) is an alumina system particle.

[Claim 4] The constituent for coatings given in any 1 term of claims 1–3 whose ** (C) are what has activity energy-line reactivity.

[Claim 5] The constituent for coatings given in any 1 term of claims 1–4 whose ** (C) are the anionic dispersants which make a quarternary–ammonium–salt radical an opposite cation.

[Claim 6] The constituent for coatings given in any 1 term of claims 1–5 to which the object base material to apply prints to the compound sheet of a plastics nature film, paper, paper, and the film made from plastics, or these.

[Claim 7] That by which spreading posture was carried out is JIS. Constituent for coatings given in any 1 term of claims 1–6 whose abrasion loss after 500 rotations is 50mg or less by 1kg load in the Taber abrasion test based on K-6902.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the constituent for coatings excellent in abrasion-proof nature. In more detail, although printed to a film, papers, those compound sheets, or these, it is related with the coating constituent which covers a front face.

[0002]

[Description of the Prior Art] In order to use the reactant resin of activity energy-line hardenability resin as a coating agent which covers front faces, such as paper and a film made from plastics, to raise the abrasion-proof nature on the front face of covering and to protect from the blemish by friction or the scratch conventionally, the coating agent which contains a hard perfect spherical particle to activity energy-line hardenability resin is advocated.

[0003]

[Problem(s) to be Solved by the Invention] However, since the manufacturing cost of a hard perfect spherical particle was usually high, a commercial item serves as an expensive rank and it was hard to use, and when coating of a hard perfect spherical particle and the mixture of reactant resin was diluted and carried out to a solvent, the sedimentation stability of a hard perfect spherical particle is poor, and there was a trouble that it was difficult to continue the stable coating.

[0004]

[Means for Solving the Problem] the result of having examined wholeheartedly the coating agent in which the coating by which the coat with abrasion-proof nature was obtained and was stabilized, without this invention persons using a hard perfect spherical particle is possible -- the bottom of specific conditions -- as a particle -- not necessarily -- true -- although it did not need to be spherical, it found out that a specific spherical thing discovered abrasion-proof nature, and this invention was reached.

[0005] That is, whenever [practical use spherical / Wadell] are 0.70-0.99, and this invention is 2 1,300-8,000kg [/mm] Knoop hardness. (B) is the constituent for coatings with which it consists of non-subtlety (particle A) activity energy-line reactivity resin (B) and a dispersant (C), and (A) is characterized by (C) being 0.2 - 10 % of the weight 45 to 95% of the weight five to 35% of the weight based on the whole weight.

[0006]

[Embodiment of the Invention] What is chosen from the group which consists of aluminas (an aluminum oxide, an aluminum hydroxide, alumina white, etc.), a zirconia (zirconium dioxide), tungsten carbide, titanium carbide, silicon carbide, boron carbide, and a diamond as (A) in this invention is mentioned. These -- one sort -- or two or more sorts may be used together. With an alumina system particle, the alumina which carried out resin coating of the front face of a silica alumina and an alumina other than an alumina shall also be included. Things desirable [among these] are aluminas and a zirconia, and especially desirable things are aluminas.

[0007] whenever [practical use spherical / Wadell of (A)] -- usually -- 0.70 to 0.99 -- desirable -- 0.80 to 0.98 -- it is 0.90-0.97 especially preferably. If whenever [practical use spherical / Wadell] becomes inadequate [the abrasion-proof nature on the front face of a coat] for it to be less than 0.70 and exceeds 0.99, the manufacturing cost of (A) will become high and the commercial-scene rationality of the constituent of this invention will be lost. In this invention, whenever [practical use spherical / all particle each] does not need to be the above-mentioned range, and should just be above-mentioned within the limits as the average. Whenever [practical use spherical / Wadell] is a value expressed with / (diameter of circle equal to the projected area of a particle) (the minimum diameter of circle circumscribed to the projection image of a particle), and a particle can be measured by carrying out electron microscope observation.

[0008] the Knoop hardness of (A) -- usually -- 1,300-8,000kg/mm² it is -- desirable -- 1,500-7,000kg/mm² it is -- especially -- desirable -- 1,700-6,000kg/mm² it is . Knoop hardness is 2 1,300kg/mm. In the following, the abrasion-proof nature on the front face of a coat becomes inadequate. Knoop hardness is 2 8,000kg/mm. What is exceeded does not exist in a nature. Knoop hardness is the minute pushing hardness measured using a Knoop indenter, and is a value expressed with the quotient which **(ed) the load when attaching the indentation of a rhombus to a trial side with the projected area of the depression searched for from the die length of the diagonal line with a longer permanent depression. This trial is ASTM. It is carried out based on C-849.

[0009] 3-50 micrometers (diameter of NASSEN Stein) of mean particle diameter of (A) used for this invention are usually 8-40 micrometers preferably. In the range whose mean particle diameter of (A) is 3-50 micrometers, the transparency of a coat, abrasion-proof nature, and surface smooth nature become good. By weight, the grain size of (A) in 1-100 micrometers is usually 90% or more, and is 95% or more preferably.

[0010] Using SK laser particle-size-distribution measuring instrument (Seishin Enterprise make), measurement of mean particle diameter adds 50-100mg of inspection samples to a dispersion medium, and measures them using the back SK laser particle-size-distribution measuring instrument to which the supersonic wave was applied for 60 seconds.

[0011] In this invention, activity energy-line hardenability resin (B) puts the thing of the resin hardened by irradiating ultraviolet rays or an electron ray, and the compound which has a radical polymerization nature double bond 1-5, or more than it in the molecular structure is used. The radical affinity double bond equivalent

contained in resin is 0.5 – 15 meq/g, and is 1 – 8 meq/g preferably. If the radical affinity double bond equivalent is 0.5 – 15 meq/g, hardenability is good, and hardening contraction is also small and can be used satisfactory as a coating constituent. Although there is especially no limitation if a thing well-known as activity energy-line hardenability resin can be used and an ethylene nature partial saturation radical is contained, with a number average molecular weight of 1,000 or less monomers and number average molecular weight 1,000 are exceeded, and 30,000 or less oligomer is mentioned.

[0012] As monomers, the following nonionic thing is specifically mentioned.

(1) The acrylate of the fatty alcohol of one to 6 organic functions of carbon numbers 2–30 (meta), or -- a carbon number -- two – 30 -- one – six -- organic functions -- fatty alcohol -- a carbon number -- two – four -- alkylene -- oxide -- one – 30 -- a mol -- an addition product -- acrylate (meta) -- (-- i --) -- a hydroxyl group -- not containing -- acrylate (meta) -- lauryl (meta) -- acrylate -- Stearyl (meta) acrylate, 1, 4-butane JIORUJI (meta) acrylate, 1, 6-hexane JIORUJI (meta) acrylate, 1, the six mol (it is called Following PO) addition product (meta) acrylate of propylene oxide of 6-hexylene glycol, Neopentyl GURIKORUJI (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, Pentaerythritol tetrapod (meta) acrylate, polyethylene GURIKORUJI (meta) acrylate (1,000 or less number-average-molecular-weight molecular weight), Polypropylene GURIKORUJI (meta) acrylate (1,000 or less number-average-molecular-weight molecular weight), the ten mol addition product Tori (meta) acrylate of trimethylol propane PO, 15 mol addition product hexa (meta) acrylate of sorbitols PO, etc.;

(ii) Hydroxyl-group content (meta) acrylate 2-hydroxyethyl (meta) acrylate, 2-hydroxy butyl (meta) acrylate, neopentyl glycol monochrome (meta) acrylate, TORIMECHI roll pro pansy (meta) acrylate, pen TAERISURITORUJI (meta) acrylate, polyethylene-glycol monochrome (meta) acrylate (1,000 or less number-average-molecular-weight molecular weight), polypropylene-glycol monochrome (meta) acrylate (1,000 or less number-average-molecular-weight molecular weight), etc.;

(2) Monochrome (meta) acrylate, such as four mol addition product (meta) acrylate of acrylate (meta) phenols EO of the 1–30 mol addition product of alkylene oxide of carbon numbers 2–4 of the phenol of one to 6 organic functions of carbon numbers 6–50, and eight mol addition product (meta) acrylate of nonyl phenol EO; di(meth) acrylate, such as four mol addition product di(meth)acrylate of bisphenol A EO, and 20 mol addition product di(meth)acrylate of PO(s) of bisphenol A;

[0013] (3) The carbon numbers 6–50 which have three to 6 membered-ring, or a ring beyond it, the alicyclic alcohol beyond it, or the acrylate (meta) cyclobutane (meta) acrylate of one to 6 organic functions of the 1–30 mol addition product of alkylene oxide of the carbon numbers 2–4, Dimethylol cyclo BUTANJI (meta) acrylate, the eight mol addition product di(meth)acrylate of dimethylol cyclobutanes EO, Cyclohexane (meta) acrylate, cyclohexane thio (meta) acrylate, Isobornyl (meta) acrylate, cyclohexane JIORUJI (meta) acrylate, Dimethylol tricyclo DEKANJI (meta) acrylate, hydrogenation bisphenol A di(meth)acrylate, the 20 mol addition product di(meth)acrylate of PO(s) of hydrogenation bisphenol A, 3, 3', 5, and 5' – tetra-hydroxyl hydrogenation bisphenol A tetrapod (meta) acrylate, 1, and

4-cyclo DODEKANJI (meta) acrylate;

(4) amide group content ethylene nature unsaturated-compound (meta) acrylamide and N-alkyl (carbon numbers 1-8) (meta) acrylamide [— for example], N, and N-dialkyl (carbon numbers 1-8) acrylamide [, such as N-methylacrylamide,] [— for example] and N-hydroxyalkyl (carbon numbers 1-8) (meta) acrylamide [— for example, [, such as N,N-dimethylacrylamide, N, and N-G n- or i-propyl acrylamide,]];N and N-dihydroxy alkyl (carbon numbers 1-8) (meta) acrylamide [, such as N-methylol (meta) acrylamide and N-hydroxyethyl (meta) acrylamide,] [— for example], such as N and N-dihydroxyethyl (meta) acrylamide, and vinyl lactams [for example, N-vinyl pyrrolidone] etc.;

[0014] (5) Amino-group content ethylene nature unsaturated-compound dialkyl (carbon numbers 1-8) amino alkyl (carbon numbers 2-10) ester, [, such as dihydroxy alkyl (carbon numbers 1-8) amino alkyl (carbon numbers 2-10) ester and morpholino alkyl (carbon numbers 1-8) ester, — for example dimethylaminoethyl (meta) acrylate, diethylamino (meta) acrylate, and morpholino ethyl (meta) acrylate,], such as dimethylaminoethyl fumarate, and heterocycle type vinyl compound [— for example], such as vinylpyridines, such as 2-vinylpyridine and 4-vinylpyridine N-vinylpyridine, and N-vinyl imidazole etc.;

(6) The acrylic ester (meta) of halogen atom content (meta) acrylate TORIBUROMO phenyl (meta) acrylate, TORIBUROMO benzyl (meta) acrylate, TORIBUROMO phenoxy ethyl (meta) acrylate, and dibromo phenyl glycidyl ether, the poly ETOKISHIJI (meta) acrylate of tetrabromobisphenol A, etc.;

(7) Other ethylene nature unsaturated-compound glycidyl (meta) acrylate, styrene (for example, styrene, vinyltoluene, etc.), allyl compounds (for example, diallyl phthalate etc.), etc.;

[0015] As oligomer, the following are specifically mentioned.

(8) polyol (for example, ethylene glycol —) with 2-6 urethane (meta) acrylate organic functions 1,4-butanediol, neopentyl glycol, polyether polyol, The poly caprolactone polyol, polyester polyol, polycarbonate polyol, A polytetramethylene glycol etc. and the organic poly isocyanate for example, tolylene diisocyanate and xylylene diisocyanate — With a number average molecular weight of 30,000 or less which is isophorone diisocyanate, hexamethylene di-isocyanate, etc. and the reactant of a hydroxyl-group content ethylene nature unsaturated compound [for example, the hydroxyl-group content (meta) acrylate of (ii) of the above (1)] etc. urethane (meta) acrylate;

(9) Polyester (meta) acrylate with polyester (meta) acrylate polybasic acid (for example, isophthalic acid, a terephthalic acid, a fumaric acid, a maleic acid, an adipic acid, etc.), and polyhydric alcohol with 2-6 functional groups [for example, the polyol indicated above (8)], two or more ester bonds obtained from an acrylic acid according to esterification and two or more ethylene nature partial saturation radicals etc.;

[0016] (10) Epoxy (meta) acrylate which is the reactant of epoxy resins, such as end glycidyl ether of an epoxy (meta) acrylate bisphenol A mold epoxy resin, a bisphenol female mold epoxy resin, the organic poly isocyanate (for example, 2, 4-tolylene diisocyanate, 2, 6-tolylene diisocyanate, etc.) conversion bisphenol A mold epoxy resin, and the bisphenol A mold propylene oxide addition product, and an

acrylic acid (meta);

(11) Butadiene polymers which have an ethylene nature partial saturation radical in a principal chain and a side chain (for example, polybutadiene etc.);

(12) The siloxane polymer which has an ethylene nature partial saturation radical in the principal chain and side chain of dimethylpolysiloxane [for example, dimethyl SHIROKISANJI (meta) acrylate] etc.; these one sort or two sorts or more can be used. Things desirable [among these] are acrylate and especially a desirable thing is the acrylate oligomer of the acrylate monomer of - (3), and (1)(9) - (11).

[0017] As a dispersant (C) used by this invention, if usually used for a coating and ink, there will be especially no limit. As an example, it is a non-reactive polymer organic system dispersant, a non-reactivity low-molecular organic system dispersant, and ionicity, and a reactant low-molecular organic system dispersant, a non-reactivity inorganic system dispersant, etc. are mentioned. As a non-reactive polymer organic system dispersant, the formalin condensate of a naphthalene sulfonate, a polystyrene sulfonate salt, a carboxymethyl cellulose, polycarboxylic acid salts (polyacrylate etc.), polyvinyl alcohol, etc. are mentioned. such weight average molecular weight -- 2,000-500,000 -- it is 3,000-200,000 preferably.

[0018] As a non-reactivity low-molecular organic system dispersant, a with a weight average molecular weight of less than 2000 thing is mentioned.

(i) -- polyalkylene glycol mold; -- the alkylene (carbon numbers 2-4) oxide (1-30 mols) addition product of the fatty alcohol of carbon numbers 4-30 -- The alkylene (carbon numbers 2-4) oxide (1-30 mols) addition product of the alkylphenol of carbon numbers 4-30, The alkylene (carbon numbers 2-4) oxide (1-30 mols) addition product of the fatty amine of carbon numbers 4-30, alkylene (carbon numbers 2-4) oxide (1-30 mols) addition product of the aliphatic series amide of carbon numbers 4-30, etc.;

(ii) -- polyhydric-alcohol mold; --, such as a fatty acid of carbon numbers 4-30, the monoester compound of a glycerol and the fatty acid of carbon numbers 4-30, the monoester compound of pentaerythritol and the fatty acid of carbon numbers 4-30, the monoester compound of sorbitol and the fatty acid of carbon numbers 4-30, and a monoester compound of SORUBITANRU

Carboxylate mold; (iii) Alkali-metal salts (the sodium, potassium, etc.), ammonium salt, quarternary ammonium salt, etc. of a fatty acid of carbon numbers 4-30;

(iv) -- sulfate mold; --, such as alkali-metal salts (the sodium, potassium, etc.), ammonium salt, quarternary ammonium salt, etc. of the fatty alcohol sulfate of carbon numbers 4-30, the fatty alcohol sulfate of carbon numbers 4-30, and the sulfate of the alkylene (carbon numbers 2-4) oxide (1-30 mols) addition product of the fatty alcohol of carbon numbers 4-30

[0019] (v) -- sulfonate mold; --, such as alkali-metal salts (sodium, potassium, etc.), ammonium salt, quarternary ammonium salt, etc., such as a sulfonic acid of the alkylphenol of carbon numbers 4-30, and a sulfonic acid of the alkylphenol of carbon numbers 4-30

(vi) -- phosphoric ester mold; --, such as alkali-metal salts (sodium, potassium, etc.), ammonium salt, quarternary ammonium salt, etc., such as fatty alcohol phosphoric-acid monoester of carbon numbers 4-30, fatty alcohol phosphoric-acid diester of carbon numbers 4-30, and fatty alcohol phosphoric-acid monoester of

carbon numbers 4-30

The 1st - a tertiary amine salt type; (vii) The inorganic-acids (hydrochloric acid etc.) salt of the monoester of the fatty acid of the aliphatic series (the class [1st] - the 3rd class) amine of carbon numbers 4-30, triethanolamine, and carbon numbers 4-30, organic acids (carboxylic acid of carbon numbers 1-4 etc.), etc.; Quaternary-ammonium-salt mold; (viii); such as quaternary ammonium salt of the fatty acid of carbon numbers 4-30 [0020] etc. It is ionicity and a with a weight average molecular weight of less than 2,000 thing is mentioned as a reactant low-molecular organic system dispersant.

(i) (meta) -- sulfate mold anionic dispersant [of AKURIRO yloxy radical content alcohol]; --; such as alkali-metal salts (the sodium, potassium, etc.), ammonium salt, quaternary ammonium salt, etc. of a sulfate of the AKURIRO (meta) yloxy radical content fatty alcohol sulfate of carbon numbers 4-30, and the AKURIRO (meta) yloxy radical content fatty alcohol of carbon numbers 4-30, such as an alkylene (carbon numbers 2-4) oxide (1-30 mols) addition product

(ii) (meta) -- phosphoric ester mold anionic dispersant [of AKURIRO yloxy radical content alcohol]; --; such as alkali-metal salts (sodium, potassium, etc.), ammonium salt, quaternary ammonium salt, etc., such as AKURIRO (meta) yloxy radical content fatty alcohol phosphoric-acid monoester of carbon numbers 4-30, AKURIRO (meta) yloxy radical content fatty alcohol phosphoric-acid diester of carbon numbers 4-30, and AKURIRO (meta) yloxy radical content fatty alcohol phosphoric-acid monoester of carbon numbers 4-30

(iii) an AKURIRO yloxy radical content cationic dispersant (meta) (an opposite anion -- a halogen anion --), for example, (meta), AKURIRO yloxy alkyl (carbon numbers 2-6) trialkyl (carbon numbers 4-30) ammonium salt A sulfuric-acid anion, a carbonic acid anion, etc.. In the ester exchange reaction object of the alkylene (carbon numbers 2-4) oxide addition product (1-100 mols) of a methyl acrylate and dialkyl (carbon numbers 4-30) amino ethanol, (Meta) By the reaction with alkylating agents, such as alkyl (carbon numbers 1-30) halide or a dialkyl sulfuric acid [, for example, AKURIROKISHIECHIRU (meta) dimethyl lauryl ammoniumchloride, such as what is obtained (Meta) As inorganic system dispersants, such as];, such as an AKURIROKISHIPUROPIRUJI ethylhexyl ammonium methosulfate, phosphoric-acid systems, such as a polyphosphate and a phosphoric acid, are mentioned.

[0021] A thing desirable [among these] is ionicity, and is a reactant low-molecular organic system dispersant, and still more desirable things are the sulfate mold anionic dispersant of AKURIRO (meta) yloxy radical content alcohol, and the phosphoric ester mold anionic dispersant of AKURIRO (meta) yloxy radical content alcohol. The 4th class trialkylammonium base is desirable as a counter ion of the anionic dispersant of the above-mentioned (meta) AKURIRO yloxy radical content. Alkyl groups are carbon numbers 1-6, and even if these are the same, they may differ. As an example of the anionic dispersant which makes a quaternary-ammonium-salt radical an opposite cation, the methyl triethyl ammonium salt of the mono-phosphoric ester of hydroxyethyl methacrylate, the methyl triethyl ammonium salt of the mono-phosphoric ester of hydroxyethyl acrylate, the triethyl ammonium salt of the mono-phosphoric ester of hydroxy butyl acrylate, the methyl

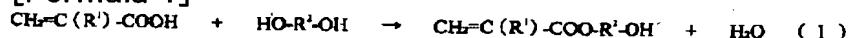
triethyl ammonium salt of the sulfate of hydroxyethyl methacrylate, the methyl triethyl ammonium salt of the sulfate of hydroxyethyl acrylate, etc. are mentioned. The quarternary ammonium salt of the mono-phosphoric ester of hydroxyethyl methacrylate is [among these] desirable.

[0022] The approach of acquiring through (i) shown below as an example – (iii) as a manufacturing method of these sulfate quarternary ammonium salt and phosphoric ester quarternary ammonium salt is mentioned.

(i) (meta) A monoester-ized reaction with an acrylic acid, alkylene (carbon numbers 2–30) diol, or a polyalkylene (carbon numbers 2–4) glycol (3,000 or less number average molecular weight) is performed. This is expressed with a general formula (1).

[0023]

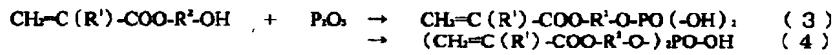
[Formula 1]



[0024] The inside of a formula, and R1 H or a methyl group is expressed. R2 An alkylene group (carbon number; 2–30) or a polyalkylene glycol (molecular weight; 3,000 or less) is expressed. This reaction (i) is performed under overalcohol (for example, 1.1–10 mols are superfluous to one mol of acrylic acids), and the unreacted object after reaction termination is removed by vacuum distillation etc. The monoester-ized reaction of the compound (one hydroxyl-group content) and acids (a sulfuric anhydride, phosphoric anhydride, etc.) which were obtained by (ii) and (i) is performed. General formula (2) This is expressed with – (4).

[0025]

[Formula 2]



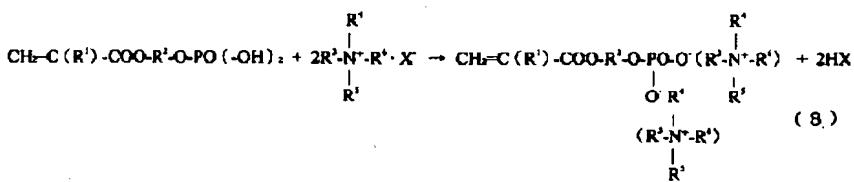
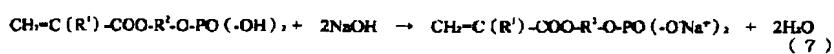
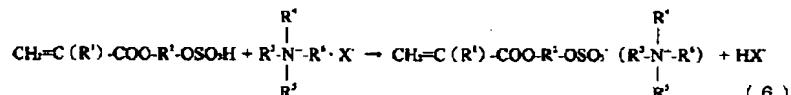
[0026] The inside of a formula, and R1 And R2 It is the same as the above.

Although some diester compound is obtained as a by-product when making it react with a phosphoric anhydride, most in a reactant is a phosphoric-acid monoester compound.

(iii) Neutralization by the bases (a sodium hydroxide, a potassium hydroxide, quarternary ammonium salt, etc.) of the compound obtained above (ii) is performed. General formula (5) This is expressed with – (8).

[0027]

[Formula 3]



[0028] The inside of a formula, and R1 And R2 It is the same as the above. R3 –R6 An alkyl group (carbon number; 1–6) is expressed. X – Cl-, Br-, CH₃ SO₄-, C₂ H₅ SO₄-, and CH₃ OCO₂ – It expresses. In this reaction (iii), the sulfuric monoester compound and phosphoric-acid monoester compound which are obtained at a reaction (ii) may be used for the constituent of this invention, as long as it is not necessary to neutralize completely and is neutralized in part by the base. The acid number of the dispersant obtained is usually 0 – 500 mgKOH/g, and is 20 – 300 mgKOH/g preferably.

[0029] The content of (A) in the constituent of this invention is usually 5 – 35 % of the weight to the sum total weight of (A) – (C), and is 10 – 25 % of the weight preferably. At less than 5 % of the weight, if the abrasion-proof nature of the paint film after hardening becomes poor and exceeds 35 % of the weight, the sedimentation stability of the particle in a coating constituent (A) gets worse, and it is not suitable as a coating constituent. The content of (B) in the constituent of this invention is usually 45 – 95 % of the weight to the sum total weight of (A) – (C), and is 70 – 92 % of the weight preferably. At less than 45 % of the weight, if the hardenability of a coating constituent becomes poor and exceeds 95 % of the weight, the design nature demanded as a coating constituent cannot be attained (paint film gloss cannot be made low). The content of (C) in the constituent of this invention is usually 0.2 – 10 % of the weight to the sum total weight of (A) – (C), and is 1 – 8 % of the weight preferably. At less than 0.2 % of the weight, if the sedimentation stability of the particle in a coating constituent (A) becomes poor and exceeds 10 % of the weight, the hardenability of a coating constituent becomes poor and it is not suitable as a coating constituent.

[0030] In this invention, other particles (D) can be blended further. Although non-subtlety particles other than (A) are mentioned and there is especially no limit of a configuration, particle size, etc. as (D), that whose mean particle diameter is usually 0.01–50 micrometers can be used, what is 0.05–30 micrometers is desirable, and it will be satisfactory if it can be used as a flattening, a bulking agent, and a pigment. For example, silicas (a fines silicic acid, a water silicic acid, diatomaceous earth, colloidal silica, etc.) A carbonates [sedimentation nature (activity, dry type, heavy, or light) calcium carbonate, silicates (a fines magnesium silicate, talc, a soapstone, and a steer light --) A calcium silicate, aluminosilicate magnesium, aluminosilicate soda, etc., carbon black (channel black, furnace black, and thermal black --)], such as chalk, such as acetylene black, **** clay, whitewash, a choke, and a magnesium carbonate, clay (the nature clay of a kaolin, the nature clay of a sericite, and the nature clay of a BAIROFI light --) aluminas (an aluminum oxide --), such as nature clay of a montmorillonite, a bentonite, and acid clay Zirconias, such as an aluminum hydroxide and an alumina white (zirconium dioxide), Aluminum sulfates (a sulfuric-acid band, a sulfuric-acid alumina, satin white, etc.) Barium sulfates (baryta powder, precipitated barium sulphate, lithopone, etc.) Gypsum fibrosum (anhydrous, half-water, etc.), the white lead, mica powder, a zinc white, titanium oxide, an activity calcium fluoride, a zeolite, cement, lime, calcium sulfite, molybdenum disulfide, asbestos, glass fiber, a lock fiber, micro balun, etc. are mentioned. Two or more sorts of these could be

used together, and two or more sorts could be compound-ized. Things desirable [among these] are silicas and carbonates. Loadings are 50 or less % of the weight based on the whole weight, and are 30 or less % of the weight preferably.

[0031] Furthermore, the additive usually added by the constituent of this invention as occasion demands at coatings, such as a photopolymerization initiator, a defoaming agent, a leveling agent, a silane coupling agent, a thixotropy nature grant agent (thickener), a slipping agent, an antioxidant, and an ultraviolet ray absorbent, and ink can be blended with arbitration. Usually, loadings are 6 or less % of the weight preferably 20 or less % of the weight to the weight of the whole constituent. As a photopolymerization initiator, a benzophenone, orthochromatic methyl o-benzoylbenzoate, 4-benzoyl-4'-methyl diphenyl sulfide, an isopropyl thioxan ton, Hydrogen length cutting die photopolymerization initiators, such as a diethyl thioxan ton and ethyl-4-(diethylamino) benzoate; Benzoin alkyl ether, Benzyl dimethyl ketal, 1-hydroxy cyclohexyl phenyl ketone, 2-hydroxy - Intramolecular cleavage mold photopolymerization initiators, such as 2-methyl-1-phenyl propane-1-ON, alkyl phenylglyoxylate, and a diethoxy acetophenone, etc. are mentioned.

[0032] As a defoaming agent, lower alcohol system defoaming agent; octyl alcohol, such as a methanol and a butanol, Higher-alcohol system defoaming agents, such as hexadecyl alcohol; Oleic acid, fatty-acid system defoaming agent [, such as stearin acid,]; -- fatty-acid-ester system defoaming agent [, such as glycerin monolaurylate,]; -- phosphoric ester system defoaming agent [, such as tributyl phosphate,]; -- calcium stearate -- Metal soap system defoaming agent;; other straight-mineral-oil system defoaming agents, such as aluminum stearate; A polyethylene glycol, Silicone system defoaming agents, such as polyether system defoaming agents, such as a polypropylene glycol, dimethyl silicone oil, alkyl denaturation silicone oil, and fluoro silicone oil, etc. are mentioned. As a leveling agent, a nonyl phenol ethyleneoxide addition product, Polyethylene-glycol type non-ion system surface active agents, such as a stearin acid ethyleneoxide addition product; Sorbitan palmitic-acid monoester, Polyhydric-alcohol type non-ion system surface active agents, such as sorbitan stearin acid monoester and sorbitan stearin acid triester; A perfluoroalkyl ethyleneoxide addition product, Fluorochemical surfactants, such as perfluoroalkyl carboxylate and a perfluoroalkyl betaine; denaturation silicone oil, such as an alkyl denaturation silicone oil and a polyether denaturation silicone oil, etc. is mentioned.

[0033] As a silane coupling agent, gamma-aminopropyl triethoxysilane, Ureido system silane coupling agents, such as amino system silane coupling agent; ureido propyl triethoxysilane, such as gamma-aminopropyl trimethoxysilane and gamma-phenylamino FUROPIRU trimethoxysilane; A vinyl ethoxy silane, vinyl methoxysilane, Vinyl system silane coupling agents, such as a vinyl tris (beta-methoxyethoxy) silane; Gamma-methacryloxypropyl trimethoxy silane, Methacrylate system silane coupling agents, such as gamma-methacryloxypropylmethyldimethoxysilane; Gamma-glycidoxypropyltrimetoxysilane, epoxy system silane coupling agent [of **]; -- isocyanate system silane coupling agent [, such as gamma-isocyanate propyl triethoxysilane,]; -- poly ethoxy dimethylsiloxane -- Polymer mold silane coupling agents, such as poly ethoxy dimethylsiloxane; cation mold silane coupling agents, such as an N-(N-benzyl-

beta-aminoethyl)-gamma-aminopropyl trimethoxysilane hydrochloride, etc. are mentioned.

[0034] As a thixotropy nature grant agent (thickener), organic system thixotropy nature grant agents (thickener), such as inorganic system thixotropy nature grant agent (thickener); hydrogenation castor oil waxes, such as a bentonite, an organic processing bentonite, and a pole detailed surface-preparation calcium carbonate, calcium stearate, aluminium oleate, and polymerization linseed oil, etc. are mentioned. As a slipping agent, silicone, such as polyolefine wax; dimethyl silicone oil, such as amount hydrocarbons; polyethylene wax [, such as metal soap; paraffin wax,] of giant molecules, such as higher-fatty-acid amides; calcium stearates, such as higher-fatty-acid ester; ethylene bis-octadecanamide, such as butyl stearate, and oleic amide, and aluminium oleate, a polypropylene wax, and carboxyl group content polyethylene wax, alkyl denaturation silicone oil, and fluoro silicone oil, is mentioned.

[0035] As an anti-oxidant, it is a triethylene glycol-screw. - [3-(3-t-butyl-5-methyl-4-hydroxyphenyl) propionate], A 1,6-hexanediol-screw [3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate], octadecyl-3- (3 and 5-G t-butyl-4-HIDOTOKISHI phenyl propionate --) Hindered phenolic antioxidants, such as 3 and 5-G t-butyl-4-hydroxybenzyl FOSUFONETO-diethyl ester; amine system antioxidants, such as n butylamine, triethylamine, and diethylamino methyl methacrylate, etc. are mentioned. As an ultraviolet ray absorbent, 2-(5-methyl-2-hydroxyphenyl) benzotriazol, 2-(3, 5-G t-butyl-2-hydroxyphenyl) benzotriazol, 2-(3, 5-G t-butyl-2-hydroxyphenyl)-5-chlorobenzo triazole, 2- Benzotriazol system ultraviolet ray absorbents, such as benzotriazol; Triazine system ultraviolet ray absorbent [, such as a 2-(4, 6-diphenyl-1,3,5-triazine-2-IRU)-5-[(hexyl) oxy-]-phenol,]; (3, 5-G t-amyl-2-hydroxyphenyl) benzophenone system ultraviolet ray absorbent [, such as a 2-hydroxy-4-n-octyloxy benzophenone,]; -- 2 -- oxalic acid anilide system ultraviolet ray absorbents, such as a - ethoxy-2'-ethyl OKISA rucksack acid bis-anilide, etc. are mentioned.

[0036] The coating constituent of this invention comes to mix the compound of above others to homogeneity (A), (B), (C), and if needed. Although there are an approach of mixing the one remaining persons, the approach of mixing three persons to coincidence, etc. after mixing inner of (A), (B), and (C) 3 person 2 persons as an approach of mixing, there is especially no limitation. The temperature at the time of mixing is usually 0-60 degrees C, is 5-40 degrees C preferably, and is 15-30 degrees C especially preferably. In order to remove the bubble produced at the time of mixing, it is desirable to mix under reduced pressure (40 or less mmHgs). As equipment to mix, they are the omnipotent mixer in which the reduced pressure in an iron pot is possible, and a planetary mixer. In case coating of the constituent of this invention is carried out to a base material, in order to adjust to the viscosity suitable for coating, it can dilute and use with one or more sorts of solvents if needed. The solvent content in a coating is 40 or less % of the weight more preferably 50 or less % of the weight from the point of coating fitness. Since desiccation does not take time amount when the solvent content in a coating is 50% or less, coating can be carried out without reducing production speed.

[0037] As this solvent, especially if a resin constituent (except for a non-subtlety particle) is dissolved, it will not be limited. Specifically For example, aromatic-hydrocarbons-solvent; ethyl acetate, such as toluene, a xylene, and ethylbenzene, An ester system or ester ethers solvents, such as butyl acetate and methoxy butyl acetate; Diethylether, A tetrahydrofuran, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, Ethers solvents, such as propylene glycol monomethyl ether and diethylene glycol monoethyl ether; An acetone, A methyl ethyl ketone, methyl isobutyl ketone, a di-n-butyl ketone, Ketones, such as a cyclohexanone; A methanol, ethanol, n-propanol, Isopropanol, n-butanol, isobutanol, t-butanol, Alcohols solvents, such as 2-ethylhexyl alcohol and benzyl alcohol; Dimethylformamide, Sulfoxide system solvents [, such as amide series solvent; dimethyl sulfoxide], such as dimethylacetamide and N-methyl pyrrolidone; water;, two or more sorts of these partially aromatic solvents, etc. are mentioned. A desirable thing is the ester solvent and alcohols solvent whose boiling point is about 70–100 degrees C among these solvents, and especially desirable things are ethyl acetate, ISOBURO pill alcohol, and such mixture. Moreover, the viscosity (under 25 degrees C) of a coating is usually 400 – 3,000 mPa·s preferably 200 to 5,000 mPa·s. When viscosity is within the limits of this, it sinks in, there are no problems, such as nonuniformity and leveling nature aggravation of a coating, and coating can be stabilized and carried out.

[0038] When carrying out coating of the constituent of this invention, coaters, such as roll coaters (size press, gate roll coater, etc.), a bar coating machine, a gravure coating machine, an air knife coating machine, and a blade coating machine, can be used. the amount of coating -- as the weight after desiccation -- usually -- 1 – 50 g/m² -- it is 3 – 30 g/m² preferably. Desiccation is performed by hot blast heating etc. Although drying temperature changes with the classes of dryer variously, 50–200 degrees C of temperature inside a dryer are usually 100–150 degrees C preferably. When coating of the constituent of this invention is carried out with these coaters, although thickness changes with coaters, it is usually 3–50 micrometers, and is 5–30 micrometers preferably.

[0039] Ultraviolet rays and an electron ray are mentioned as an activity energy line given to the constituent of this invention by which coating was carried out. When making it harden by ultraviolet rays, the well-known black light equipped with the high pressure mercury vapor lamp, the metal halide lamp, etc. can be used. The exposure of the ultraviolet rays at the time of hardening is 50 – 2,000 mJ/cm² preferably. the coating film hardened when it became insufficient [less than two 50 mJ/cm] hardening an exposure and it exceeded 2,000 mJ/cm² -- yellowing -- it may deteriorate When making it harden with an electron ray, well-known electron-beam-irradiation equipment can be used. The exposure of an electron ray is 1 – 10Mrad preferably. The coating film or base materials (paper, film, etc.) which were hardened when it became insufficient [less than 1 Mrad] hardening an exposure and it exceeded 10Mrad may receive damage, and may deteriorate.

[0040] Evaluation of abrasion-proof nature is JIS. According to K-6902, it shall evaluate by performing the Taber abrasion test.

Taber abrasion test method;

(1) Create the hardening film to a base material by carrying out coating of the

constituent used for this invention to a base material, and irradiating an activity energy line.

(2) Stick this on the board which carried out adhesion processing, and cut it off in 10cmx10cm magnitude. Let this be a test sample.

(3) JIS The Taber abrasion test is performed according to K-6902. The abrasion loss after 500 rotations is measured by 1kg load. The mass of a test sample is measured to mg unit before the trial, the mass of the test sample after a trial is measured, and the abrasion loss of a coating is computed. The abrasion loss of the coating of this invention is usually 50mg or less, and is 40mg or less preferably.

[0041] As an object base material with which the coating which consists of a constituent of this invention is applied, although there is especially no limitation, the compound sheet of the film made from plastics, paper, paper, and the film made from plastics or the thing which printed to these is mentioned. concrete -- for example, products made from plastics, such as a vinyl chloride sheet, a polyethylene film, and polyester film, -- papers [, such as films; tissue paper, papers strengthening paper, titanium paper, a latex impregnated paper and stencil paper for plaster board,]; -- what printed to these compound sheet and these is mentioned. The constituent of this invention is very advantageous as a coating agent which protects these object base materials. front faces covered with the constituent of this invention, such as a film made from plastics, and paper, -- abrasion-proof nature -- excelling -- friction -- it scratches, and is hard to attach **** and an appearance is also still better. Since it has this effectiveness, especially the constituent of this invention is very useful as a coating agent which protects printed printing sides, such as plastic film and paper. As these applications, many applications, such as interior material (interior etc.), sheathing materials (a housing wallplate, vehicle wallplate, etc.), a film, and wrapping, are presented. A building-materials application and housing interior material (furniture, such as a wallplate, and a table, a desk, a bookcase, a built in kitchen unit), and vehicle interior material are especially suitable.

[0042] Although an example explains this invention below, this invention is not limited to this. The section in an example shows the weight section.

[0043] The phosphoric-acid monoester 1,000 section of hydroxyethyl methacrylate is taught into the glass reactor equipped with the example of manufacture 1 dropping funnel, the thermometer, and the stirring rod, and temperature control is carried out to 25 degrees C. It is dropped at the bottom of stirring, applying [MONOMECHIRUTORI ethylammonium methyl carbonate 435] it for 60 minutes. Since carbon dioxide gas begins to occur as MONOMECHIRUTORI ethylammonium methyl carbonate is dropped, dropping is continued taking care that a reaction does not overrun recklessly. After continuing stirring after dropping termination for 90 minutes, it decompressed by 20 or less mmHgs for 20 minutes. Let this thing be a dispersant 1. The acid number of this dispersant was 270 mgKOH/g.

[0044]

example 1 NEOMA BA-641 [the Sanyo Chemical Industries [, Ltd.] make and bisphenol A (EO)4 diacrylate] 60.0 section NEOMA TA-401 [the Sanyo Chemical Industries [, Ltd.] make and a trimethylol-propane (EO) 3 thoria chestnut rate] 20.0 section Hari Mick AX-116[-- whenever [the Micron make, mean-particle-

diameter:25micrometer, Knoop hardness 2,800, and / practical use spherical / Wadell] -- fused-alumina] of 0.97 15.0 section IRUGA cure 184 [the Ciba-Geigy make and a photopolymerization initiator]

4.0 section Aerosil 200 [the product made from Japanese Aerosil, and a thixotropy nature grant agent]

1.0 section ethyl acetate 30.0 partial powder 1 These were mixed to homogeneity with the planetary mixer the 1.0 sections, and the constituent of this invention was obtained. This thing was coated so that it might become the vinyl chloride sheet which printed with 25 micrometers in desiccation thickness, and ultraviolet rays (UV) were irradiated two times 500 mJ/cm. The abrasion loss in the above-mentioned Taber abrasion test was 35mg.

[0045]

Example 2 NEOMA BA-641 64.0 section NEOMA TA-401 20.0 section Hari Mick AX-116 15.0 section Aerosil 200 1.0 section ethyl acetate 30.0 partial powder 1 These were mixed to homogeneity with the planetary mixer the 1.0 sections, and the constituent of this invention was obtained. This thing was coated so that it might become polyester film which printed with 25 micrometers in desiccation thickness, and 5Mrad exposure of the electron ray (EB) was carried out. The abrasion loss in the same Taber abrasion test as an example 1 was 30mg.

[0046] As shown in one to examples 3-5 and example of comparison 7 table 1, the constituent was created, and in the case of UV irradiation, it carried out like the example 1. In EB exposure, it carried out like the example 2. The result was indicated to Table 1. In addition, front Naka and the following were used.

Hari Mick C100-32; Micron make, mean particle diameter: Whenever practical use [of 6 micrometers, Knoop hardness 2,800, and Wadell] spherical, it is fused-alumina SUMIKO random AA-18 of 0.96.;

The Sumitomo Chemical [Co., Ltd.] make, mean particle diameter: Whenever practical use [of 0.80 alumina alumina X; mean-particle-diameter:15micrometer, Knoop hardness 2800, and Wadell] spherical [, and], it is the crushing indeterminate form alumina [0047] of 0.65. [practical use / of 18 micrometers, Knoop hardness 2800, and Wadell]

[Table 1]

	実施例					比較例					
	1	2	3	4	5	1	2	3	4	5	6
ネオマー BA-401	60	64	64	53	53	60	64	64	35	64	25
ネオマー TA-401	20	20	20	17	17	20	20	32	14	20	10
ハリミック AX-116	15	15	—	25	—	—	—	3	50	15	—
ハリミック C100-32	—	—	15	—	—	—	—	—	—	—	45
スミコランタム AA-18	—	—	—	—	25	—	—	—	—	—	—
アクリルX	—	—	—	—	—	15	15	—	—	—	—
イソカーボン7 184	4.0	—	—	—	—	4.0	—	—	—	—	—
アクリル 200	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
酢酸エチル	30	30	30	30	30	30	30	30	30	30	30
分散剤 1	1.0	1.0	1.0	5	5	—	—	1.0	1.0	0.1	20
合計(重量部)	131	131	131	131	131	130	130	131	131	130.1	150
塗膜乾燥厚み (μ m)	25	30	25	25	25	25	25	25	25	25	25
照射	UV	EB	EB	EB	EB	UV	EB	EB	EB	EB	EB
摩耗量 (mg)	35	30	25	15	20	XX	XX	XX	10	35	25

[0048] In addition, front Naka and abrasion loss XX show that even the base material was shaved off.

[0049]

[Effect of the Invention] The coating constituent of this invention does the following effectiveness so.

(1) Since it excels in sedimentation stability when it dilutes with a solvent etc. to the viscosity which is easy to carry out coating, it excels in coating fitness, and the coating coat of the stable quality can be obtained industrially.

(2) front faces covered with the coating constituent of this invention, such as a film made from plastics, and paper, -- abrasion-proof nature -- excelling -- friction -- scratch, it is hard to attach *** and an appearance is also still better.

[Translation done.]

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